LOW-TEMPERATURE LUMINESCENCE IN Cu_6PS_5Br SUPERIONIC CRYSTALS

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Photoluminescence (PL) spectra of Cu_6PS_5Br crystals are studied in a broad spectral range (0.5–2 μm) at 77 K, under various excitation conditions. In the PL spectra a number of bands of different origin is revealed. The computer processing of the spectrum is carried out and the mechanisms of the radiative recombination resulting in the band appearance, are discussed. The comparative analysis of the PL and optical absorption spectra is performed.

INTRODUCTION

Cu_6PS_5Br crystals of argyrodite type are known as fast-ion conductors and ferroelastics [1]. The fundamental absorption edge of these crystals was studied in detail in a broad spectral and temperature range [2–4]. At low absorption levels ($\alpha < 150$ cm^{-1}) the absorption edge is formed by indirect electron-phonon transitions [2], and at high absorption levels (200 cm^{-1} $< \alpha <$ 2000 cm^{-1}) and low temperatures in the range of direct optical transitions exciton bands are observed, exhibiting the series of "allowed" *s*-excitons of Wannier-Mott type [3]. The increase of temperature results in the exciton bands smearing and at $T \geq 200$ K at the absorption edge only exponential parts are observed, their temperature and spectral behaviour being described by Urbach's rule. In [4] the exciton luminescence at 77 K was reported, correlating well with the exciton absorption spectrum. However, no detailed PL studies in a broad spectral range were performed.

EXPERIMENTAL

For the experimental studies Cu_6PS_5Br single crystals, obtained by chemical vapour transport [1], were used. It should be noted that at room temperature the crystals belong to the cubic syngony (space group *F43m*) and at $T < 102$ K – to the monoclinic syngony (space group C_c) [1]. The PL spectra were studied at various excitation conditions, using an Ar^+ (λ = 476.5 nm), *He-Cd* (λ = 440.7 nm) and a nitrogen pulsed (λ= 337 nm) lasers. The spectra were measured by SDL-1, DFS-24 and MDR-3 diffraction spectrometers. The crystal was mounted in a UTREX cryostat, providing the temperature stabilizing within 0.1 K.

RESULTS AND DISCUSSION

In the PL spectra of Cu_6PS_5Br, shown in Figs. 1 and 2, at 77 K a number of bands of different intensities and widths is observed as sharp peaks and shoulders. The PL spectrum, obtained under pulsed laser excitation, looks rather complicated. After the necessary computer processing and fitting it revealed to be a superimposement of seven bands whose energy positions, widths, relative intensities and contour areas are listed in the general Table. The observed bands can be divided into several groups depending on the mechanism of the radiative recombination. The long-wavelength group of E_1 to E_6 (the notions of the bands in Figs. 1 and 2 correspond to those in the Table) broad bands results from the recombination of free and bound

to a local centre charge carriers ("band-to-local centre" transitions). The narrowest E_9 band corresponds to the annihilation of the free exciton in the ground state (n = 1). Accordingly, the exciton absorption band is located at 2.327 eV [4].

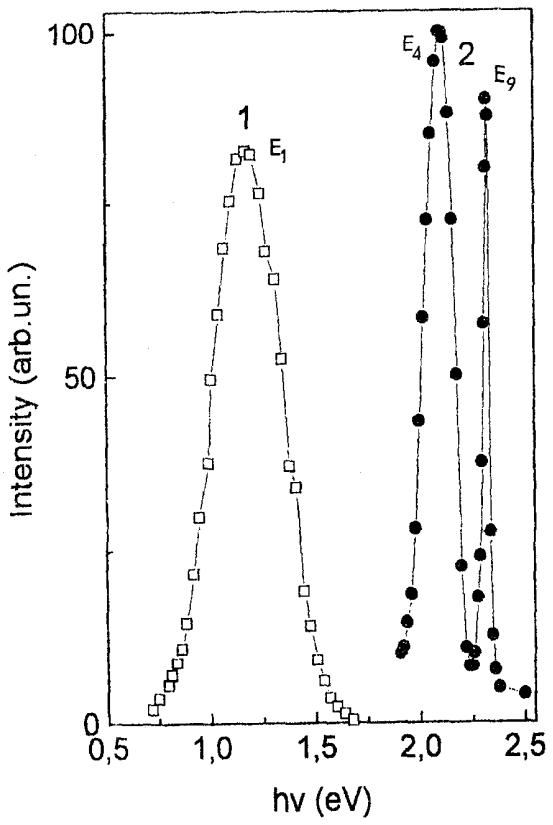

Fig. 1. Unpolarized PL spectra of Cu_6PS_5Br crystal at 77 K obtained under the excitation by *He-Cd* (λ=440.7 nm) (1) and Ar^+ (λ=476.5 nm) (2) lasers.

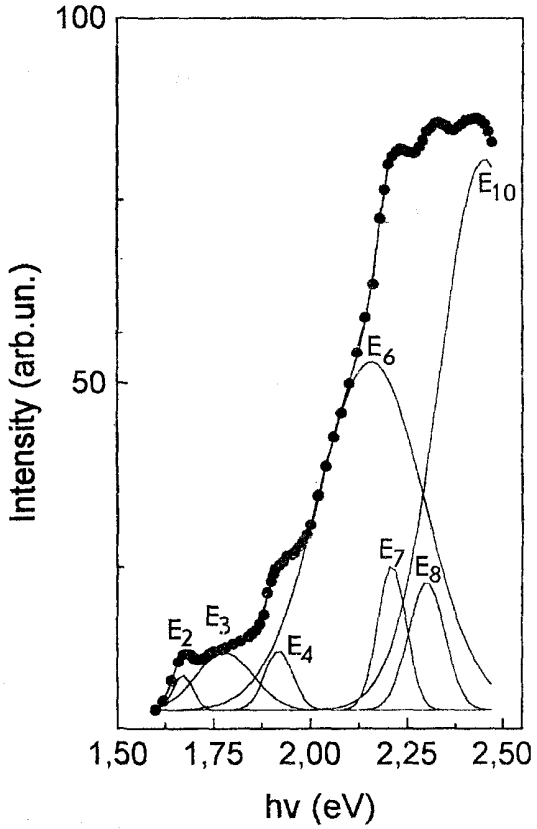

Fig. 2. Unpolarized PL spectra of Cu_6PS_5Br crystal at 77 K obtained under the excitation by pulsed nitrogen laser (λ=337 nm).

Now consider the origin of E_7, E_8 and E_{10} bands, being revealed under pulsed nitrogen laser excitation. The energy position of the E_7 band correlates well with the indirect gap value E_g^i = 2.193 eV [2], therefore it corresponds to the indirect interband transition. The E_8 band is of the same nature as the E_9 band. The stronger Stokes shift of the E_8 band relatively to that of the E_9 can be the result of the higher excitation power provided by the pulsed nitrogen laser ($(3–5)\times10^9$ W/pulse). The mechanism leading to the $E_{10} > E_g^d$ band appearance is probably related to the surface recombination of free electrons and holes as well as free copper atoms. It should be also noted that no bands corresponding to the direct interband transition, have been observed in the PL spectra (the direct gap width, determined from the exciton absorption spectrum, is given in the Table and equals to 2.341 eV [4]).

Table. Energy positions, widths, relative intensities and contour areas of the PL spectrum bands of Cu_6PS_5Br crystals.

Peak	Transition	Luminescence				Excitonic absorption	E_g^i	E_g^d
E_i	$E_i \rightarrow E_j$	Center (eV)	Height (a.u.)	Area (a.u.)	Width (eV)	E_{exc} (eV)	(eV)	(eV)
E_1	$E_1 \rightarrow E_v$ $E_c \rightarrow E_1$	1.179	84.11	34.11	0.324	-	-	-
E_2	$E_2 \rightarrow E_v$	1.671	3.78	0.312	0.052	-	-	-
E_3	$E_3 \rightarrow E_v$	1.779	6.21	1.44	0.148	-	-	-
E_4	$E_4 \rightarrow E_v$	1.919	6.43	0.73	0.072	-	-	-
E_5	$E_5 \rightarrow E_v$	2.095	7.93	16.27	0.133	-	-	-
E_6	$E_6 \rightarrow E_v$	2.157	37.8	16.29	0.274	-	-	-
E_7	$E_c^i \rightarrow E_v$	2.210	15.77	1.83	0.074	-	2.193	-
E_8	$E_{exc} \rightarrow E_v$	2.300	13.93	2.07	0.095	-	-	-
E_9	$E_{exc} \rightarrow E_v$	2.322	79.17	2.56	0.026	2.327	-	-
								2.341
E_{10}	$E_{10} \rightarrow E_v$	2.450	59.90	22.01	0.234			

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НИЗЬКОТЕМПЕРАТУРНА ЛЮМІНЕСЦЕНЦІЯ СУПЕРІОННИХ КРИСТАЛІВ Cu_6PS_5Br

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Досліджені спектри фотолюмінесценції кристалів Cu_6PS_5Br в широкому спектральному діапазоні (0.5 – 2 мкм) при температурі 77 К та різних умовах збудження. Обговорюються механізми випромінювальної рекомбінації, що приводять до виникнення смуг різної природи, виявлених у спектрах фотолюмінесценції. Проведено порівняльний аналіз спектрів фотолюмінесценції та оптичного поглинання.